

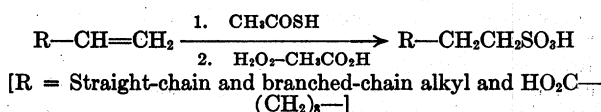
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Preparation of Sulfonic Acids from Unsaturated Compounds¹

Sulfonic acids have been prepared in good yield from a series of 1-olefins and also from oleic and 10-hendecenoic acids by free radical addition of thiolacetic acid to form thiolacetates, followed by hydrogen peroxide-acetic acid oxidation. This reaction sequence permits the preparation of isomer-free terminal sulfonic acids from 1-olefins. A method of purifying 1-olefins by a partial, selective epoxidation procedure has also been described. It has been shown for the first time that methyl esters are obtained in high yield by reaction of sulfonic acids with diazomethane. Reaction paths for the oxidation of thiolacetates to sulfonic acids are discussed.

Sulfonic acids are a well known class of compounds whose preparation and properties have been thoroughly studied.^{3,4} Surprisingly, there is no general synthesis of sulfonic acids that does not involve isolation of a salt (Pb^{+2} , Ba^{+2} , Ca^{+2}), followed by a precipitation of the cation with a suitable anion (SO_4^{-2} , Cl^-) or by ion exchange.

As an adjunct to other work in our laboratory, isomer-free terminal sulfonic acids were prepared from 1-olefins by a new preparative route. This procedure involved the free-radical addition of thiolacetic acid to the desired 1-olefin to give a terminal thiolacetate,⁵ followed by oxidation with hydrogen peroxide (92–93%) and acetic acid directly to the terminal alkanesulfonic acid in high overall yield, as illustrated:



The reaction sequence was also applied to several nonterminal unsaturated compounds, such as cyclopentene, cyclohexene, and methyl oleate with equally good results, but in the last case a mixture of isomeric sulfonic acids is obtained because the unsaturated compound is not symmetric.

Experimental

Purification of 1-Olefins.—Advantage was taken of the much faster rate of epoxidation of an internal double bond

compared with that of a terminal double bond to perform a selective, partial epoxidation.

Commercial peracetic acid (30% in acetic acid) was added dropwise in a 1:1 mole ratio to a commercial sample of terminal olefin which contained some nonterminal olefin. The stirred reaction mixture was maintained at 25–30° for 2.5 to 6 hr., depending upon the olefin and amount of nonterminal isomer. Good temperature control was important to moderate the exothermic reaction of the peracetic acid with the olefin and the subsequent neutralization of the reaction mixture with base.

Water (1–2 l.) was added to the reaction flask to halt the reaction, and cold base (6 N NaOH) was then added dropwise to the reaction mixture over a period of 0.5 to 0.75 hr. until it was weakly basic, the temperature being kept between 20 to 25° throughout. As neutrality was approached, foaming occurred which was broken by agitation. (Care must be taken to avoid too rapid addition of base which sends the temperature out of control and causes unreacted peracetic acid to react vigorously with 1-olefin.)

The organic layer was separated with no attempt to break any emulsion present, and it was washed with saturated salt solution until neutral. Excess base was then neutralized to decrease foaming that occurs during subsequent steam distillation, and the mixture was then added to water (2–3 l.) and steam distilled until either the water being co-distilled with the olefin brought the latter over yellow or the organic phase stopped codistilling (as was the case with the short-chain olefins). The steam distillation separated the unoxidized 1-olefin from emulsion and from most of the products of epoxidation (epoxide, glycol, hydroxyacetate, and polymer). The organic layer in the steam distillate was separated and dried successively with sodium sulfate and calcium sulfate. The olefin was then analyzed for oxirane content (hydrobromic acid-acetic acid).⁶ In most cases, after epoxidation, washing and steam distillation, the olefin contained less than 2% epoxide. This amount of epoxide was removed by fractional distillation of the 1-olefin. A visual inspection of the pot residue after fractional distillation of the olefins always revealed a white gelatinous material which is believed to be polymer formed from the epoxide. Oxirane analyses of the fractionally distilled olefins showed them to be oxirane-free.

(1) Paper VI in the series "Organic Sulfur Derivatives." Paper V is *J. Org. Chem.*, **23**, 1525 (1958).

(2) Eastern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

(3) C. M. Suter, "The Organic Chemistry of Sulfur," John Wiley and Sons, Inc., New York, 1944, p. 94 *et. seq.*

(4) M. Quaedvlieg, "Methoden der Organischen Chemie," Vol. IX, 4th Ed., G. Thieme Verlag, Stuttgart, 1955, pp. 347–405.

(5) See N. H. Koenig and D. Swern, *J. Am. Chem. Soc.*, **79**, 362, 4235 (1957), for leading references to earlier literature.

(6) A. J. Durbetaki, *Anal. Chem.*, **28**, 2000 (1956).

TABLE I
THIOLACETATES, R-S-COCH₃

R—	B.p., °C/mm.	n _D	Yield %	Carbon		Hydrogen		Sulfur	
				Calcd.	Found	Calcd.	Found	Calcd.	Found
CH ₃ (CH ₂) ₄ —	78–83/20	1.4580 ^b	88	57.51	57.25	9.65	9.73	21.89	22.15
CH ₃ (CH ₂) ₅ —	...	1.4592 ^b	80	59.97	59.75	10.07	9.88	19.97	19.79
CH ₃ (CH ₂) ₆ —	116/23	1.4580 ^c	73	62.04	61.50	10.41	10.25	18.37	18.43
CH ₃ (CH ₂) ₇ —	132/24	1.4586 ^c	91	63.79	63.67	10.71	10.53	17.00	16.97
CH ₃ (CH ₂) ₈ —	164/27	1.4602 ^c	86	66.62	66.74	11.18	11.29	14.80	14.62
CH ₃ (CH ₂) ₁₁ —	120–123/0.3	1.4613 ^c	80	68.81	68.42	11.55	11.17	13.09	12.79
CH ₃ (CH ₂) ₁₃ —	122/0.08	1.4625 ^c	84	70.54	70.39	11.84	11.86	11.75	11.87
CH ₃ (CH ₂) ₁₅ —	28–30 ^a	...	56	71.95	71.70	12.08	11.77	10.64	10.45
CH ₃ (CH ₂) ₁₇ —	38–38.5 ^a	...	60	73.10	72.32	12.27	12.20	9.76	9.59
HOCO(CH ₂) ₁₀ —	52–54 ^a	...	61	59.96	60.38	9.29	9.59	12.32	12.01
CH ₃ (CH ₂) ₃ CH(CH ₃)CH ₂ —	82–86/17	1.4592 ^b	82	59.97	59.56	10.07	9.88	19.97	20.06
(CH ₃) ₂ CH(CH ₂) ₃ —	90–91/19	1.4572 ^b	86	59.97	59.96	10.07	9.97	19.97	19.91
(CH ₃) ₃ CCH ₂ CH(CH ₃)CH ₂ —	109–111/25	1.4583 ^c	86	63.79	63.57	10.71	10.57	17.00	16.97
Cyclopentyl	79–82/20	1.4914 ^b	76	58.31	58.00	8.39	8.24	22.26	22.26
Cyclohexyl	90–91/15	1.4946 ^b	84	60.74	60.52	8.92	8.76	20.23	19.68
CH ₃ (CH ₂) _{15–x} CH(CH ₂) _x COOCH ₃ ^d	100/0.001	1.4669 ^c	70	67.70	67.71	10.82	10.84	8.59	8.73

^a M.p. Fisher-John's block. ^b 25°. ^c 30°. ^d x = 7 or 8.

The infrared absorption band at 968 cm.⁻¹, characteristic of the *trans* configuration of a nonterminal olefin, was the main criterion for measuring the purity of the terminal olefin. The intensity of the 968 cm.⁻¹ band both before and after epoxidation indicated that the internal olefin content of the purified 1-olefin was much less than 1% (no observable band in 0.05-mm. liquid film). Since the *cis* form is the less stable configuration of the nonterminal olefin and is more reactive to epoxidation than the *trans* isomer, reliance can be put on the spectroscopic data as a measure of both the *cis* and *trans* isomers. Gas-liquid chromatography supplemented the infrared with respect to purity of the olefin both before and after the selective, partial epoxidation.

The above general procedure was used in the purification of all the commercial terminal olefins studied (C₇, C₁₀, C₁₂, C₁₄, C₁₆, and C₁₈). There were small differences in the procedures depending upon the chain length and amount of non-terminal olefin present. The apparent reactivity of olefins with peracetic acid decreased from C₇ to C₁₈; it is thought that this is related to a change in solubility in the reaction mixture. It was necessary, therefore, not only to treat the higher olefins at a higher temperature (30° rather than 25°) but also for a longer time. For instance, with the C₇ olefin, the reaction time was 2 hr. and the temperature was 25°. With the C₁₀ olefin, however, about 5 hr. of reaction time was needed to remove completely the nonterminal olefin, particularly since it contained a much larger percent of non-terminal olefin than any of the others. In either of the above cases, both too long a reaction time and too high a temperature led to wasteful formation of a higher percent of epoxide.

With all the olefins except 1-heptene, only a small amount of epoxide came over during the steam distillation. Often, and particularly with the more prolonged steam distillations, several fractions had to be collected after the yellow distillate appeared in order to obtain a good yield. It was possible, however, as in the case of the C₇ olefin, to remove a larger quantity (2–4%) of epoxide by letting the steam-distilled olefin react with sodium methoxide solution (5–10 mole % of sodium, based upon olefin, dissolved in 1–2 l. of methanol) for about 15 hr., stirring if the mixture was heterogeneous. The methanol solution was poured into water (1–2 l.) and the organic layer washed several times with water. The olefin was next washed with dilute hydrochloric acid, then with water until neutral, dried over sodium sulfate and calcium sulfate, and then finally fractionally distilled.

The time required for steam distillation in proceeding from C₇ to C₁₈ increased from several hours to 16 hr. The C₇ and C₁₀ olefins could be steam distilled by the *in situ* generation of steam but those from C₁₂ to C₁₈ could be efficiently distilled only by external generation of steam. During the steam distillation of the higher molecular weight

olefins, the heterogeneous mixture in the pot often jelled. This made distillation difficult but not impossible.

Other Starting Materials.—Cyclohexene and cyclopentene were the best commercial grades (99 + mole %). 10-Hendecenoic acid and methyl oleate were of comparable purity.

Thiolacetates (Table I).—Freshly redistilled commercial thiolacetic acid (b.p. 88–92°) was added dropwise to the stirred, purified unsaturated compound in a quartz three-neck flask, the entire operation being conducted under nitrogen, while the flask was irradiated at a distance of 1 in. by a 140-watt ultraviolet lamp (high pressure quartz-mercury arc). The mole ratio of thiolacetic acid to unsaturated compound varied from 1:1 to 1:2 depending upon the availability of the olefin. Since the reaction is exothermic, it was convenient to add the thiolacetic acid through the condenser. Loss of very volatile olefins was minimized by using ice water in the condenser. The addition reaction required from 2 to 6 hr.

If the product were a liquid, the total reaction mixture was flash distilled to remove the starting materials, and then the crude thiolacetate was fractionated. If the product were a solid (adduct from 1-hexadecene, 1-octadecene, and 10-hendecenoic acid), any volatile materials were removed under vacuum and the residue was recrystallized from acetone. The yields and physical constants are listed in Table I, along with the analytical data. Although some of these compounds are known in the literature, they are reported again here because of their high purity, especially in the case of the terminal thiolacetates.

Sulfonic Acids (Table II).—The following reaction conditions are typical: 1-Acetylthiohexadecane (5.00 g., 0.0166 mole) and acetic acid (25 ml.) were stirred and heated at 60°. Hydrogen peroxide (93%; 3.03 g., 0.0830 mole) was added very slowly. If the addition is too rapid, the reaction temperature rises swiftly and uncontrollably owing to the catalytic effect of sulfonic acid produced. After heating for about 15 hr. (the oxidation is largely complete within 1 hr.; reactions were run overnight for convenience and to insure complete oxidation) at 65–70°, the total reaction mixture was lyophilized to obtain 1-sulfohexadecane as a fine, very hygroscopic tan solid in quantitative yield. The crude reaction product was recrystallized from petroleum ether (b.p. 60–70°, 12 ml./g.) to give white needle-like crystals (m.p. 72.5–73.0°).

The crude oxidation products all showed very weak carbonyl bands at 1740 cm.⁻¹ and 1720 cm.⁻¹ suggesting small amounts of carboxylic acid and aldehyde. These probably come from carbon-sulfur bond cleavage and further oxidation.

All of the sulfonic acids were found to be very difficult to

TABLE II
SULFONIC ACIDS

Name	Melting ^a point	Carbon ^d		Hydrogen ^d		Sulfur ^d		Neut. equiv. ^d	
		Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
1-Sulfo-2-methylpentane	67-69° ^b	43.35	44.70	8.49	8.81	19.29	19.15	166	187
1-Sulfododecane	49-52°	57.56	57.67	10.46	10.58	12.81	12.31	250	290
1-Sulfotetradecane	64-65.5°	60.38	60.38	10.86	11.23	11.52	11.63	278	263
1-Sulfohexadecane	72.5-73°	62.71	63.26	11.19	11.73	10.44	9.74	306	307
1-Sulfooctadecane	64-70°	64.63	62.67	11.45	11.67	9.57	9.37	334	348
11-Sulfohendecanoic acid	67.5-80°	49.61	49.59	8.33	8.37	12.01	12.00	133	143
9(10)-Sulfooctadecanoic acid	... ^c	59.31	58.19	9.96	9.88	8.78	8.91	182	183

^a Extent of hydration unknown; this may account for wide melting range in some cases. ^b B.p. at 0.002 mm. ^c Oxidation was conducted on methyl 9(10)-acetylthiooctadecanoate, but product obtained was the sulfocarboxylic acid instead of the expected sulfo ester. The oxidation product was analyzed directly. ^d The difficulty in obtaining concordant analytical results on free sulfonic acids is discussed in Experimental.

TABLE III
METHYL SULFONATES, RSO₂OCH₃

Ester	M.p.	Carbon		Hydrogen		Sulfur	
		Calcd.	Found	Calcd.	Found	Calcd.	Found
Methyl 2-methylpentanesulfonate	... ^a	46.64	46.93	17.79	17.68	8.94	9.01
Methyl dodecanesulfonate ^b	34.0-34.5°	59.05	59.03	10.67	10.87	12.13	12.60
Methyl tetradecanesulfonate ^b	39.8-40.0°	61.55	62.00	11.09	11.28	10.96	11.03
Methyl hexadecanesulfonate ^c	47.7-47.9°	63.70	63.94	11.32	11.40	10.00	10.00
Methyl octadecanesulfonate ^c	54.9-55.1	65.46	66.09	11.57	11.86	9.20	9.17
Methyl (11-methylsulfo)hendecanoate ^b	37.0-37.8°	53.03	53.45	8.90	9.12	10.89	10.94
Methyl 9(10)-methylsulfooctadecanoate	... ^d	61.18	61.43	10.27	10.35	8.17	7.88

^a B.p. 59-64° at 0.15 mm., *n*_D²⁰ 1.4336. ^b Recrystallized from acetone at -30°. ^c Recrystallized from ethanol at 4°. ^d B.p. 190-196° at 0.05 mm., *n*_D²⁰ 1.4550.

analyze by combustion because of, in part, their marked hygroscopicity so that some of the analytical data (Table II) are not as good as would be desired. All sulfonic acids were converted to the corresponding methyl esters, however (Table III), and excellent analytical data were then obtained.

Preliminary studies using commercial peracetic acid (40%) for oxidation of thiolacetates showed that the sulfonic acid discolored and charred because of sulfuric acid present in the peracid. Peracetic acid was also prepared from hydrogen peroxide and acetic acid using a strong acid ion exchange resin. The sulfonic acid prepared from the sulfuric acid-free peracetic acid was light colored, but this added another stage to the oxidation procedure and increased the amount of material to be lyophilized. Direct oxidation of thiolacetate with hydrogen peroxide alone was possible but temperature control was difficult, stirring was poor and the quality of the sulfonic acid was low.

Methyl Sulfonates (Tables III).—Excess ethereal diazomethane was added portionwise to an ether solution of the sulfonic acid at 0°. After standing for several hours, the solvent was removed and the residue put on a short chromatographic column containing Florosil. The column was eluted with a small amount of petroleum ether (b.p. 60-70°) to remove any polymethylene and then with benzene to remove the methyl sulfonate. Unchanged acid remained on the adsorbent. The eluted methyl sulfonate was then recrystallized from acetone or ethanol. Methyl 2-methylpentanesulfonate and dimethyl 9(10)-sulfooctadecanoate were distilled; the former was not chromatographed first.

Discussion

The extensive work on the direction of free radical addition to a double bond has been summarized by Walling.⁷ Terminal addition of a radical to a double bond will predominate over nonterminal addition by a factor between 50 and 1000. Thus,

the thiolacetate obtained from the addition of thiolacetic acid to a 1-olefin will have a minimum purity of 98% with respect to terminal isomer and probably will be better than 99%.

Since this path provides a highly selective route to thiolacetate, it was necessary to have a source of isomer-free 1-olefin. Commercially available 1-olefins contain varying amounts of internal and branched olefins. Therefore, it was necessary to develop a procedure for obtaining pure 1-olefin.

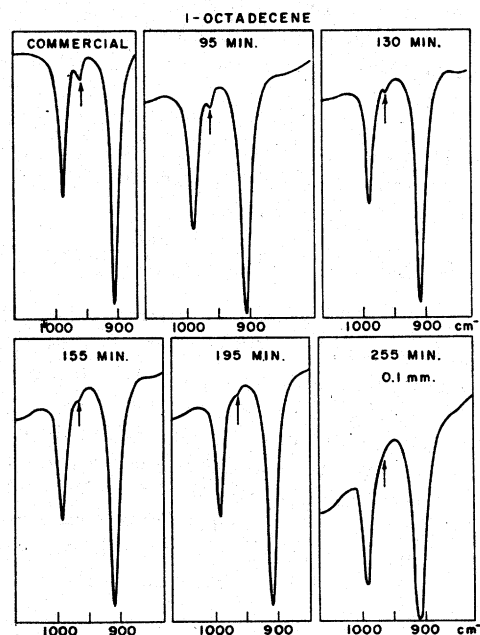


Fig. 1.—Effect of time on completeness of epoxidation of internal olefins in commercial 1-octadecene.

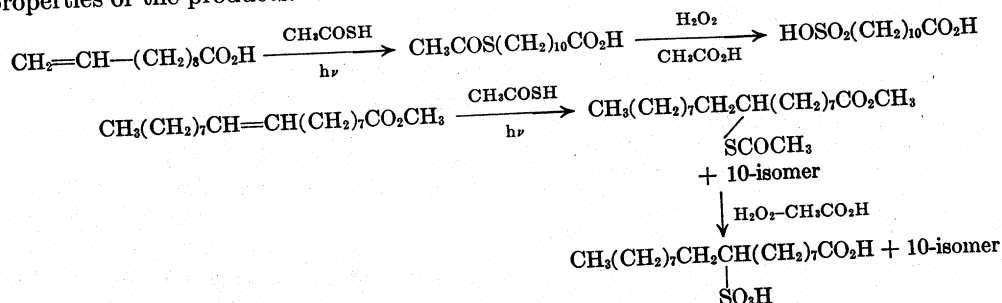
cis- and *trans*-Disubstituted ethylenes are epoxidized approximately 20–30 times more rapidly than are monoalkylethylenes (1-olefins).⁸ The partial, selective epoxidation of the undesired internal olefin is possible, therefore, at a sacrifice of some of the desired 1-olefin. The change in concentration of internal olefins as a function of time of partial epoxidation of commercial 1-octadecene is shown in Figure 1. In the figure, the gradual disappearance of the 968-cm.⁻¹ band due to the *trans* internal isomers of octadecene is compared to the 910- and 990-cm.⁻¹ bands of 1-octadecene. The relevant portion of the infrared spectrum of commercial 1-decene is shown before and after treatment (Figure 2). This particular olefin was the most impure with respect to internal isomers of any of the commercial olefins purified. These results, coupled with gas-liquid chromatographic analysis, indicate that the olefin is free of internal olefinic impurities.

Addition of thiolacetic acid to the purified 1-olefins gives good yields of pure thiolacetates (55–91%). Table I lists the individual yields and physical properties of the products. Some of these

taminated with a small quantity of alkane carboxylic acid (band in infrared at 1740 cm.⁻¹) due apparently to a minor amount of carbon-sulfur cleavage. Recrystallization of the sulfonic acid eliminates this minor impurity.

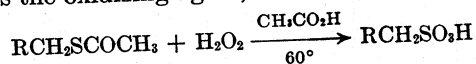
The sulfonic acids are highly hygroscopic, particularly in the finely divided form obtained by lyophilization. This characteristic, plus a tendency to be electrostatic, makes them difficult to handle and maintain in a high state of purity. The recrystallized sulfonic acids were well defined solids and they were somewhat less hygroscopic because of less surface. When 1-sulfohexadecane was exposed to atmospheric moisture, there was a very rapid uptake of moisture followed by a longer slower absorption. The absorption of water stopped and then increased or decreased depending upon the relative humidity. These results suggest that reported melting points and compositions of the so-called hydrates of sulfonic acids are artifacts.

Two sulfonic acid derivatives of long-chain aliphatic acids were prepared—11-sulfohendecanoic acid and 9(10)-sulfooctadecanoic acid:



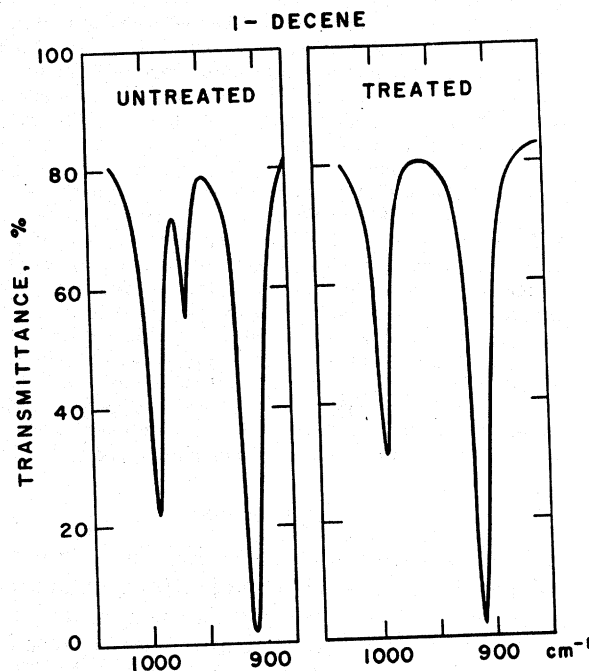
compounds have already been described in the literature, but because of the high purity of the starting materials used in this study, they are reported again here.

Thiolacetates were oxidized directly to sulfonic acids in excellent yield with 90+ % hydrogen peroxide and acetic acid (peracetic acid formed *in situ* is the oxidizing agent):

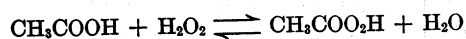


This reaction is highly exothermic and requires carefully controlled addition of the concentrated hydrogen peroxide. Also, since the product of the oxidation reaction is a strong acid which catalyzes the formation of peracetic acid, the rate of oxidation increases after some sulfonic acid has formed. Thus it is desirable to run the oxidation reaction at a slightly elevated temperature so that the hydrogen peroxide is rapidly consumed and does not accumulate and then subsequently react in an uncontrolled way.

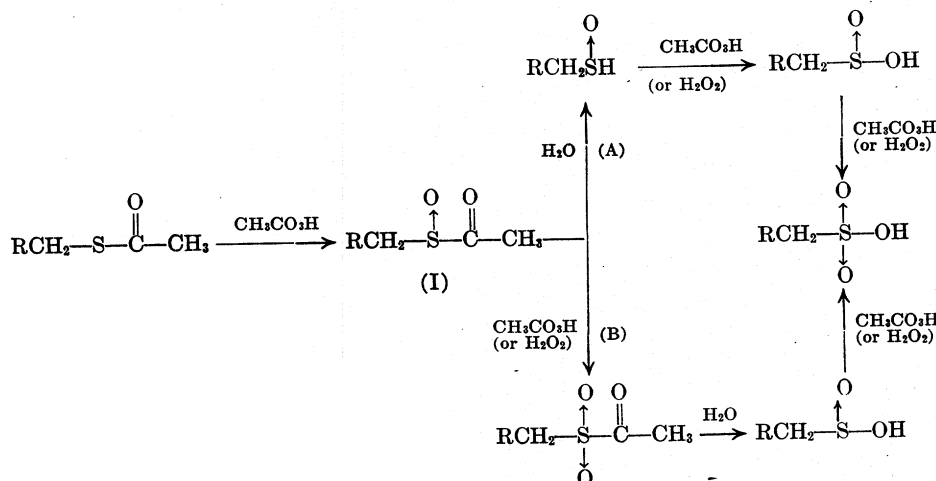
After the oxidation reaction is complete, lyophilization of the reaction mixture yields essentially pure sulfonic acid as a nonvolatile residue, con-



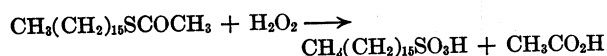
The path of oxidation of thiolacetates with hydrogen peroxide was examined. The actual oxidation is carried out in acetic acid to permit smooth control of temperature and good stirring. This suggests that the effective oxidizing agent may be peracetic acid formed by the reaction between acetic acid and hydrogen peroxide:



The oxidation of 1-hexadecanethiol by hydrogen


$$\begin{array}{ccc} \text{CH}_3(\text{CH}_2)_{15}\text{SH} + \text{H}_2\text{O}_2 & \xrightarrow{60^\circ} & [\text{CH}_3(\text{CH}_2)_{15}\text{S}]_2 \\ & \searrow 90^\circ & \downarrow 90^\circ, \text{H}_2\text{O}_2 \\ & & \text{CH}_3(\text{CH}_2)_{15}\text{SO}_3\text{H} \end{array}$$

Under more vigorous conditions (90°), the sulfonic acid is formed from both the thiol and the disulfide. At 60° with equimolar quantities of thiol and acetic acid, with hydrogen peroxide, sulfonic acid is obtained. When 1-hexadecylthiolacetate is oxidized at 60° by hydrogen peroxide alone, a short induction period is observed and then a vigorous reaction gives the sulfonic acid:

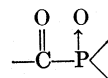


sulfonic acid formed acts as a catalyst for peracid formation from hydrogen peroxide and acetic acid. Oxidations using preformed peracetic acid, prepared with an ion exchange resin catalyst and hence free of strong acid, as expected, show no induction period.

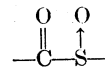
Control experiments in which water has replaced hydrogen peroxide (acetic acid present) do not cause hydrolysis of 1-hexadecylthiolacetate to the thiol. Addition of 1-sulfohexadecane to this reaction mixture, however, produces some thiol (3%). These facts suggest that the thiol is probably not an intermediate in the oxidation to the sulfonic acid since the reaction cannot be controlled by the slow hydrolysis step.⁹

The following reaction path is consistent with the above experimental facts:

The intermediate I, an acyl sulfoxide, may react by path A and/or B. Path A alone seems the more probable in view of the known hydrolytic instability of acylphosphonates, a structure



analogous to the

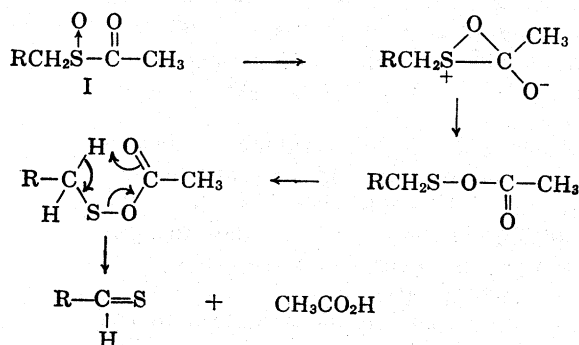
group.¹⁰

Further oxidation of the acyl sulfoxide, I, should be more difficult than oxidation of the starting thiolacetate because of the increased electronegativity of the sulfur atom. Path A would yield a

(9) Hydrolysis of the thiolacetate as the first step in the conversion to sulfonic acid cannot be ruled out unequivocally. As a referee points out, the fact that a strong acid and a little water produce some thiol might not imply that the rate of hydrolysis is slow but that the equilibrium is not very favorable in excess acetic acid. Rapid removal of thiol by oxidation would remove the equilibrium concentration which would then be resupplied by hydrolysis. In a system with little or no water and strong acid present initially, the rate would increase as hydrogen peroxide gives water and the sulfo acid.

(10) B. Ackerman, T. A. Jordan, C. R. Eddy, and D. Swern, *J. Am. Chem. Soc.*, **78**, 4444 (1956).

sulfenic acid,¹¹ a class of compounds of known facile oxidizability. The intermediate acyl sulfoxide, I, could rearrange by an intramolecular path:



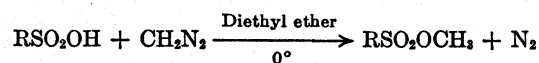
The thioaldehyde, RCHS, could be the source of

(11) N. Kharasch, S. J. Potempa, and H. L. Wehrmeister, *Chem. Rev.* **39**, 269 (1946).

the small amount of carboxylic acid, RCO₂H, that is formed.

All attempts to detect intermediate stages of oxidation failed. The oxidation of the thiolacetate was carried out with only one-third of the required hydrogen peroxide. Only one-third of the expected sulfonic acid was formed along with unchanged starting material; no intermediates could be detected by ultraviolet and infrared analysis.

Surprisingly, the reaction between sulfonic acids and diazomethane to give methyl sulfonates is not reported in the literature:



The reaction is rapid, smooth, and gives high yields of methyl esters. Some polymethylene is produced in a competing reaction but this byproduct can be conveniently separated by column chromatography, along with traces of unchanged sulfonic acid.